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THE ROLE OF SURFACE CHEMICAL ANALYSIS IN A STUDY TO SELECT REPLACEMENT PROCESSES FOR TCA VAPOR DEGREASING

Michael W. Lesley
Science and Engineering Analytical Laboratories Department
Thiokol Corporation
P.O. Box 707, M/S 245
Brigham City, Utah 84302

Lawrence E. Davis, John F. Moulder and Brad A. Carlson
Physical Electronics Laboratories
6509 Flying Cloud Drive
Eden Prairie, Minnesota 55344

ABSTRACT

The role of surface-sensitive chemical analysis (ESCA, AES, and SIMS) in a study to select a process to replace 1,1,1 - trichloroethane (TCA) vapor degreasing as a steel and aluminum bonding surface preparation method is described. The effort was primarily concerned with spray-in-air cleaning processes involving aqueous alkaline and semi-aqueous cleaners and a contamination sensitive epoxy-to-metal bondline. While all five cleaners tested produced bonding strength results equal to or better than those produced by vapor degreasing, the aqueous alkaline cleaners yielded results which were superior to those produced by the semi-aqueous cleaners. The main reason for the enhanced performance appears to be a silicate layer left behind by the aqueous alkaline cleaners. The silicate layer increases the polarity of the surface and enhances epoxy-to-metal bonding. On the other hand, one of the semi-aqueous cleaners left a nonpolar carbonaceous residue which appeared to have a negative effect on epoxy-to-metal bonding. Differences in cleaning efficiency between cleaners/processes were also identified. These differences in surface chemistry, which were sufficient to affect bonding, were not detected by conventional chemical analysis techniques.

1.0 INTRODUCTION

Currently, Thiokol Corporation Space Operations relies on vapor degreasing processes using 1,1,1 - trichloroethane (TCA) for precision cleaning of steel and aluminum parts of NASA's Space Shuttle Redesigned Solid Rocket Motor (RSRM). The purpose of these cleaning operations is to prepare the surfaces of the parts for adhesive bonding and external painting. Because TCA is an ozone depleting chemical (ODC) which will not be available after 1995, it has become necessary to identify alternative cleaning processes which produce adhesive-to-metal bond strengths which are at least as good as those produced by the baseline TCA process.

An effort has been made to understand the effects of the new cleaning processes on the metal surface chemistry (e.g. residues left by cleaners, effect on oxide composition and thickness, cleaning efficiency for process soils, etc.). If bonding data follow the same trends as surface chemistry, the amount of confidence one can have in such data is increased. This increases one's assurance that bond strength differences between cleaners are real and are not the result of anomalies in the bonding tests.

In this paper the use of surface chemical analysis techniques in the initial stages of a program to develop alternatives to TCA vapor degreasing is described. The analytical techniques used were electron spectroscopy for chemical analysis (ESCA), Auger electron spectroscopy (AES), and static secondary ion mass spectrometry (static SIMS). These methods are sensitive to changes in the top atomic layers in a surface and, as shown herein, provide unique insights into the effects of the various cleaners on adhesive bonding.

2.0 EXPERIMENTAL

ESCA, static SIMS, and AES measurements were performed at Physical Electronics Laboratories in Eden Prairie, Minnesota. The ESCA and SIMS measurements were made on a Physical Electronics Model 5600 XPS Spectrometer with a model 3700 static SIMS attachment. AES depth profiles were performed on a Physical Electronics Model 650 Scanning Auger Microprobe.

In the ESCA experiments, the sample was irradiated with monochromatic Al Kα X-radiation ($h\nu$ = 1486.6 eV) while the kinetic energies of emitted photoelectrons, from which core-level binding energies are calculated, were measured. Analyses were performed on a 4 x 10 mm rectangular area on each sample. The average analysis depth in ESCA experiments is about 30 Å, or roughly ten atomic layers. Information about surface elemental composition and chemical state (i.e. types of compounds present) can be obtained from the binding energies associated with the peaks in the spectrum.

In static SIMS measurements, an approximately 5 mm square area was bombarded with 4 keV Xe^+ ions, with masses of the resulting positive and negative secondary ion fragments measured by a quadrupole mass spectrometer. The primary ion dose used in the experiments (5×10^{12} ions/cm^2) is low enough to ensure that nearly every Xe^+ ion strikes an undamaged area of the surface and produces fragments which accurately reflect the molecular structure of the surface species. Static SIMS complements ESCA measurements and often provides more precise identification of organic compounds than is possible by ESCA alone. Static SIMS is somewhat more surface-sensitive than ESCA, with a typical analysis depth of 3 - 10 Å.

AES was performed by bombarding the surface with a finely focused 8 keV electron beam and measuring the kinetic energies of emitted Auger electrons. AES provides surface elemental compositions with a sampling depth similar to that in ESCA, but with much better lateral resolution. The electron beam can be rastered over a surface, just as in a scanning electron microscope, providing elemental dot maps and SEM micrographs. AES was used for depth profile measurements to determine oxide thicknesses. These were made by first taking a 1000 X secondary electron micrograph, an average AES scan to determine elements present, and dot maps to determine element lateral distributions. Three small (10 μm square) areas, selected to avoid areas with high levels of grit blast sand, were depth profiled by sputter etching with an Ar^+ ion beam at a rate of 30 Å/minute (calibrated against a SiO_2 film of known thickness) while AES analysis was performed on the three areas.

Metal coupons (D6AC steel and 7075 aluminum) were prepared for subsequent contamination and cleaning treatments by a standard procedure involving TCA vapor degreasing, followed by a heavy zirconium silicate gritblasting, a second TCA vapor degreasing treatment, and finally a light, "cosmetic" zirconium silicate gritblast just before processing. This procedure has been found to yield consistent, repeatable bonding characteristics. The metal coupons were processed under the same conditions as a set of bonding specimens so that surface chemistry and bond strength could be directly correlated.

The overall ODC elimination program is a cooperative venture between two Thiokol laboratories. Three-fifths of the bonding and surface analysis specimens described in this paper were processed at the Thiokol Science and Engineering (S & E) Research and Development Laboratory in

Utah, while the rest were processed at the Thiokol Huntsville Space Operations (HSO) laboratory in Huntsville, Alabama. Differences in operating parameters and how the work was divided between laboratories will be discussed later.

3.0 RESULTS AND DISCUSSION

3.1 Overview of Testing Logic

Down-select 150 → 15 cleaners. At the beginning of the program, samples of about 150 cleaners (organic solvents, aqueous alkaline cleaners, and semi-aqueous cleaners) were obtained and evaluated. Organic solvents were to be used in spray-under-immersion (SUI) cleaning processes followed by a clean solvent rinse. Aqueous alkaline cleaners or semi-aqueous cleaners can be used in a SUI process or spray-in-air (SIA) process followed by a water rinse. The initial list of 150 cleaners was reduced to 15 by such criteria as solubility of process soils (e.g. grease, oil) in the cleaners, contact material compatibility, and bonding tests. Surface analysis was not involved in this phase.

Down-select 15 cleaners/2 processes → 5 cleaners/1 process. Next, a series of bonding tests accompanied by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy/energy-dispersive X-ray analysis (SEM/EDX), and diffuse reflectance infrared spectroscopy (DRIR) surface cleanliness measurements, was performed to evaluate the 15 cleaners (equally divided between organic, aqueous alkaline, and semi-aqueous categories) applied under both SIA and SUI conditions. The role of ESCA, AES, and SIMS surface analysis in this phase was limited to characterization of cleaner residues. This consisted of evaporating a few drops of each cleaner on aluminum foil and analyzing the residues with ESCA and static SIMS. This simple, inexpensive technique can yield a great deal of information on a cleaner. One semi-aqueous cleaner left a fluorocarbon residue (possible bonding release agent !). Another organic cleaner left an excessively thick nonvolatile residue which was thick enough (tens of Å or more) to cause concerns about interference with adhesive bonding.

The organic solvents were eliminated from consideration because of poor cleaning efficiency for process soils (as determined by DRIR) and poor epoxy-to-metal bond strengths. SIA cleaning was demonstrated to be superior to SUI cleaning for semi-aqueous and aqueous cleaning. Five cleaners (three aqueous and two semi-aqueous) were selected for further study in SIA cleaning processes. SEM/EDX, FTIR, and DRIR did not detect differences in surface chemistry between samples which had been contaminated with process soils and cleaned with the aqueous and semi-aqueous cleaners. These tests were repeated in the next phase with the same result, i.e. all semi-aqueous and alkaline aqueous candidates cleaned process soils to levels below detection limits, and no cleaner-induced changes in surface chemistry were noted.

Down-select 5 → 2 cleaners. Here the main task was to down-select from the 5 SIA cleaners selected above to two cleaners which would be then subjected to extensive optimization studies. The semi-aqueous cleaners were Du Pont Axarel 52 Cleaning Agent and Dow Prima Clean Semi-Aqueous Cleaner. The aqueous alkaline cleaners were Brulin 815 GD, Metalube 4U Multi-Purpose Cleaner-Degreaser, and Jettacin (Diversey). Surface analysis began to find extensive application in the study at this point.

One objective of the surface analysis studies was to determine what the cleaners themselves do to the surfaces -- what residues they leave behind before and after rinsing, and their effect on oxide thickness and composition. A second objective was to make a preliminary determination of how well the cleaning processes remove soils which come into contact with the steel and aluminum bonding surfaces during RSRM manufacturing. These were Conoco HD-2 grease, which is applied to both steel and aluminum surfaces as a preservative, Magnaflux Magnaglo 20B magnetic particle premix and

Magnaglo WA-4 water conditioner, which are used in magnetic particle inspection of steel hardware, and Shell Diala oil, which is used as a pressure test fluid on steel parts.

Processing on semi-aqueous cleaners (Axarel 52 and Prima Clean) was handled by the S & E laboratory along with one aqueous cleaner (Jettacin, initially considered to be a semi-aqueous cleaner). The HSO laboratory processed the aqueous cleaners Brulin 815 GD and Metalube 4U. Processing conditions used at the S & E laboratory were a 30 % cleaner concentration in water (thought to be appropriate for semi-aqueous cleaners), 135 °F cleaner temperature, and a 70 psi cleaning/water rinsing pressure. At HSO, the parameters used were a 10 % cleaner concentration in water (thought to be appropriate for aqueous cleaners), a 135 °F cleaner temperature, a 1000 psi cleaning pressure, and a 70 psi rinse pressure. The reader should keep in mind that in the study to be described Axarel 52, Jettacin, and Prima Clean coupons were processed differently from the Brulin 815 GD and Metalube 4U coupons.

3.2 Typical ESCA, AES, SIMS Data

Figure 1 shows typical ESCA spectra for freshly grit blasted D6AC steel. The low-resolution "survey" scan, taken to determine what elements were present, shows components of the grit blast sand (Zr, Si, Ti, Ca, and Al). A high-resolution scan of the carbon (1s) region is also shown. The high resolution scans allow one to ascertain what sorts of compounds are present. High-resolution scans were taken on at least one characteristic peak of each element detected.

Figure 2 shows a typical AES depth profile (etch rate 30 Å/min) of freshly grit blasted D6AC steel with minor elements deleted for clarity. Also shown is the method of determining oxide thickness, i.e. by measuring the position of the "knee" of the iron level vs. sputter time curve. (The oxygen level never goes to zero because of the presence of embedded particles of zirconium silicate.) The oxide thickness in this case is about 50 Å.

Figure 3 shows typical static SIMS data (positive ions) for freshly gritblasted D6AC steel. These surfaces are quite clean as they exhibit mainly peaks of the metal and gritblast media.

3.3 Effect of Cleaners on D6AC Steel/7075 Aluminum (No Soils Applied)

Effect of Rinsing Failure. Experiments were performed in which the cleaners were applied to uncontaminated D6AC steel coupons using the SIA cleaning process and dried with no rinsing step. The purpose of such experiments was to determine what would happen in the event of a total rinsing failure. ESCA and static SIMS measurements were performed and ESCA results are given in Table I.

All cleaners leave significant residues (primarily carbonaceous) relative to freshly grit blasted steel. In the case of Jettacin, Brulin 815 GD, and Metalube 4U the layer is thick enough to almost totally suppress the Fe signal from the substrate. This indicates that the layer is on the order of at least tens of Angstroms thick and is likely to interfere with most adhesive bonds. In addition to the carbonaceous residues, the Axarel 52 surface contained significant levels of phosphates which probably are corrosion inhibitors. The Prima Clean coupon was visibly rusted, which may be due to the lack of a corrosion inhibitor as suggested by the ESCA data. Jettacin leaves sulfates, silicates, sodium, and an organic nitrogen species. Brulin 815 GD leaves organic nitrogen, phosphates, potassium, and silicate. Metalube 4U leaves sodium and silicates. The apparent alkaline nature of the deposits from Brulin, Jettacin, and Metalube in particular may have an adverse effect on metal-to-epoxy adhesion, not to mention corrosion problems, if the residues are not adequately removed by rinsing.

Residues Left After Rinsing. To determine what kinds of residues are left after rinsing, freshly grit blasted steel and aluminum coupons were cleaned by the SIA process, rinsed, dried, and subjected to ESCA and static SIMS analysis. (As with the unrinsed panels, the Prima Clean washed D6AC steel panel was visibly rusted.) Figure 4 shows ESCA carbon levels after rinsing as a function of cleaner for steel and aluminum, with the freshly grit blasted and TCA vapor degreased steel data shown for purposes of comparison. All of the cleaners except Axarel 52 on steel and aluminum and Prima Clean on steel leave a clean surface from a carbon contamination standpoint, with carbon levels similar to freshly grit blasted and TCA vapor degreased samples. Axarel 52, on the other hand, leaves a substantial carbonaceous deposit on both steel and aluminum which is not removed by a water rinse.

There is another significant difference between the alkaline cleaners and semi-aqueous cleaners which is displayed in Figure 5, a plot of Si/Zr ratio vs. cleaner for freshly grit blasted coupons which were SIA cleaned with the various cleaners and rinsed. The chart shows significantly higher amounts of surface silicon on coupons cleaned with the aqueous alkaline cleaners Jettacin, Metalube 4U, and Brulin 815 GD. (The Si/Zr atom ratio was plotted to eliminate the effect of variability in the amount of embedded $ZrSiO_4$ grit blasting sand on the apparent surface Si content.) High resolution ESCA scans and static SIMS analysis indicated that the excess silicon is present in the form of a silicate. The silicate levels seem to be highest for Metalube, with Brulin 815 GD the lowest and Jettacin in between, and the effect is stronger for aluminum than it is for steel.

Oxide Thickness Measurements. AES depth profiles were performed on steel and aluminum coupons which were cleaned, rinsed and dried with no precontamination, and also on freshly grit blasted controls and freshly grit blasted controls which had been TCA vapor degreased. With Axarel 52 cleaned samples, the AES dot maps revealed that the carbon coverage detected in the ESCA/SIMS results was non-uniform and "patchy" ; depth profiles were performed on "clean" areas in between the patches of carbonaceous material. The results for oxide/silicate overlayer thickness are displayed in Figure 6. The Prima Clean steel sample was visibly corroded as with the identically processed ESCA/SIMS sample above and, accordingly, the measured oxide thickness on the sample was greater than 300 Å. Apart from that, the cleaning treatments do not significantly increase the steel oxide thickness relative to the baseline TCA vapor degreasing process. With aluminum, all of the cleaners oxidize the surface somewhat, with Prima Clean having the greatest effect.

3.4 Cleaning Efficiency Studies

Cleaning efficiency studies were also performed to make a preliminary assessment of the ability of the cleaners to remove HD-2 grease from steel and aluminum, magnetic particle materials from steel, and Diala oil from steel. The contaminants were applied to the surfaces and placed into the various cleaning processes, and then subjected to a final rinse. In the case of Magnaflux materials, the steel coupons were treated with a solution of Magnaglo 20B magnetic particle premix solution and then rinsed with a solution of Magnaglo WA-4 water conditioner prior to cleaning. It must be remembered that these studies are not conclusive as to which cleaners are most efficient as each cleaner was tested under only one set of processing parameters, and the processing conditions were not the same for all cleaners.

In all data presentations on cleaning efficiency below, the results of the same cleaning/rinsing experiment on a sample with no precontamination (see section 3.3 above) are included so that the reader can judge how much of a particular contaminant can be attributed to the cleaner itself and how much is a result of unremoved soils. Comparative data on the TCA vapor degreasing process are also presented.

HD-2 Grease on Steel and Aluminum. ESCA cleaning efficiency results for HD-2 grease on steel and aluminum are shown in Figures 7 and 8. The ESCA carbon level is a measure of how much grease is left on the surface after cleaning. None of the cleaning treatments, except possibly Axarel 52 on steel and aluminum, and Prima Clean on aluminum, completely remove HD-2 grease. With Axarel 52 on both steel and aluminum, the static SIMS spectra of the cleaned surface indicate that the carbon residues left after cleaning originate with the cleaner. The carbon levels are actually lower when a surface is precontaminated with HD-2 grease and then cleaned with Axarel 52 than when initially noncontaminated samples are cleaned with Axarel 52. The HD-2 grease overlayer may partially prevent the components of Axarel 52 from adhering to the surface. In the case of Prima Clean on steel, the sample did not rust as was observed in the case of samples with no precontamination, suggesting that the small amount of grease left behind protects the steel from corrosion.

Static SIMS spectra of HD-2 grease precontaminated/cleaned surfaces for all cleaners except Axarel 52 contained high molecular weight (60 - 100 amu) fragments which were not present in spectra of initially uncontaminated samples which had been cleaned with the cleaners and rinsed. These fragments are indicative of HD-2 grease. An extreme example of this is given in Figure 9, which shows a static SIMS spectrum for D6AC steel which has contaminated with HD-2 grease, cleaned with Metalube 4U, and rinsed, and a spectrum of pure HD-2 grease. The cracking pattern of the carbonaceous contaminant on the HD-2 contaminated, cleaned surface matches that of HD-2 grease. It does not match the static SIMS spectra of Metalube residues.

Magnetic Particle Inspection Materials on Steel. In Figures 10 and 11, static SIMS and ESCA cleaning efficiency data for magnetic particle inspected surfaces are shown. Studies of control dried samples of Magnaglo 20B and WA-4 water conditioner indicated that the residues are primarily carbonaceous, so the ESCA carbon percentage is used as a measure of surface cleanliness. The other elements found to be present in 20B particle premix and WA-4 rinse residues (B, N, Na) were effectively removed by the rinsing techniques. All cleaning treatments effectively remove the organic component (Figure 11) except Brulin 815 GD. Static SIMS spectra (Figure 10) show that the cracking pattern of the residue left after Brulin cleaning has characteristics similar to that of a pure WA-4 rinse conditioner control.

Diala Oil on Steel. ESCA showed that all cleaners effectively removed Diala oil (data not shown). In the case of Prima Clean, the cleaning was thorough enough so that the steel sample rusted. With Axarel 52, as before, the cleaner left a heavy carbonaceous deposit of its own.

3.5 Comparison with Surface Free Energy and Bonding Data

Surface Free Energy. Contact angle measurements (using a variety of liquids of various polarities) were made on initially uncontaminated metal specimens which had been cleaned with the various cleaners, rinsed, and dried. The work of adhesion W_{ad} of a liquid can be expressed in terms of contact angle θ by the Young-Dupré equation:

$$W_{ad} = \gamma_l (1 + \cos\theta) \qquad (1)$$

where γ_l is the interfacial free energy of the liquid-vapor interface. For polar systems it is also customary to express the surface free energy γ_s as the sum of a contribution from London dispersion forces (γ^d) and polar forces (γ^p). The work of adhesion is customarily expressed in terms of dispersion and polar forces in the following manner:

$$W_{ad} = 2(\gamma_l^d\gamma_s^d)^{0.5} + 2(\gamma_l^p\gamma_s^p)^{0.5} \qquad (2)$$

So, by combining equations (1) and (2), and using contact angle data from a wide variety of liquids of known γ_l^d and γ_l^p, the contributions to surface free energy from dispersion and polar forces can be calculated.

Figure 12 shows the polar contribution to the surface free energy γ_s^p for initially uncontaminated steel and aluminum surfaces which have been cleaned with the cleaners and rinsed. Data from freshly grit blasted surfaces, and surfaces which have been TCA vapor degreased, are included for comparison. It is seen that the semi-aqueous cleaner Axarel 52 produces a highly nonpolar surface for both steel and aluminum, probably as a result of the carbonaceous residue the cleaner leaves behind. TCA vapor degreasing also lowers the surface polarity relative to freshly grit blasted material. The aqueous cleaners Jettacin, Brulin, and Metalube increase the surface polarity, most likely due to the increased silicate content. For a polar adhesive such as an epoxy, we might expect the adhesive to wet the Jettacin, Brulin, and Metalube surfaces better, resulting in better bond integrity, while with the Axarel 52 cleaner we might expect less efficient wetting and poorer epoxy-to-metal adhesion performance.

<u>Adhesion performance tests.</u> Most bonding tests were concerned with bond strength of Hysol EA-913NA epoxy adhesive to gritblasted D6AC steel or 7075 aluminum bondlines. These bondlines are much more sensitive to contamination than others on the RSRM. Bonding tests on more robust bondlines (e.g. NBR rubber-to-metal) cleaned with the five cleaners tended to fail cohesively in the rubber. The EA-913NA to metal bondlines, as expected, proved to be much more sensitive to changes in surface chemistry as shown below. Tests conducted on these were fracture toughness (tapered double cantilever beam or TDCB) and tensile adhesion. Only fracture toughness results on samples which had been contaminated with HD-2 grease, cleaned, and then rinsed will be presented. Tensile adhesion tests generally showed the same trends, but the differences were less pronounced. Fracture toughness is a more discriminating test for this type of system.

Figures 13 and 14 show the EA-913NA bond strength results for steel and aluminum along with results from HD-2 contaminated/TCA vapor degreased surfaces and data from freshly gritblasted surfaces with no grease contamination. All five cleaners perform as well as or better than the baseline TCA process for these bondlines, with the aqueous cleaners (Jettacin, Brulin 815 GD, and Metalube 4U) outperforming the semi-aqueous cleaners Axarel 52 and Prima Clean. (Note: in current practice the EA-913NA to metal bondlines receive a post-clean grit blast prior to application of the adhesive, so the relatively poor bond strength of the TCA vapor degreased specimens is not characteristic of flight hardware. Also, the relative performance of the TCA vapor degreased specimens in tensile adhesion tests is better than in the fracture toughness tests.)

The enhanced performance of the aqueous cleaners correlates with the high surface polarity, which in turn is probably caused by the silicate layer left by the cleaners. This enhancement yields higher bond strengths than a freshly grit blasted surface, and occurs despite the presence of residual HD-2 grease as detected by ESCA and static SIMS. Axarel 52, which creates a nonpolar surface as a result of the carbonaceous residues it leaves behind, does not perform as well as the aqueous cleaners. It was found that a post-clean grit blast to remove the residues was necessary to achieve high bond strengths with Axarel 52. With the aqueous cleaners, on the other hand, a post-clean grit blast actually reduced bond strength. This reduction probably occurs because of the removal of the cleaner-induced silicate layer, which apparently has beneficial effects on epoxy-to-metal adhesion.

<u>Down-select decision and work in progress.</u> At the end of the five cleaner evaluation, it was decided to proceed with further studies on Brulin 815 GD and Jettacin and to eliminate the other cleaners from consideration. Prima Clean was eliminated on the basis of the observed corrosion problems, while Axarel 52 was rejected on issues such as the necessity of a post-clean grit blast to achieve high bond strengths and seriously reduced performance of the cleaner when soil-loaded.

Jettacin, on the other hand, produced the highest bond strengths in the screening program, while Brulin was judged to be the least corrosive of the cleaners in electrochemical tests on steel. Both cleaners showed adequate soil-loaded cleaning ability in preliminary tests.

An additional testing effort to directly compare Brulin 815 GD and Jettacin is now in progress. It includes a two-level fractional factorial study which will determine the effect of such variables as wash and rinse pressures, cleaner concentration/temperature, and lab location on bond strength and surface chemistry.

4.0 SUMMARY AND CONCLUSIONS

The results here show the value of ESCA, AES, and static SIMS for explaining differences in adhesion performance for a contamination-sensitive epoxy-to-metal bondline. Conventional chemical analysis techniques failed to detect differences in surface chemistry among aqueous and semi-aqueous cleaners which in turn had measurable effects on bond strengths. These differences in surface chemistry were readily detected by ESCA, AES, and SIMS. For less contamination sensitive bondlines on the RSRM, such as the vulcanized steel-to-NBR interfaces, the differences in surface chemistry had no effect on bonding results. For such systems conventional techniques are more useful. For example, FTIR and DRIR are capable of easily discerning grease levels which will cause the robust NBR-to-steel bondline to fail.

While all five cleaners provided bond strengths equal to or better than those obtained by vapor degreasing, the aqueous cleaners (Jettacin, Metalube 4U, and Brulin 815 GD) yielded better bond strengths for an epoxy-to-metal bonding system than did the semi-aqueous cleaners (Prima Clean, Axarel 52). The reason for the difference was found to be a silicate layer left behind by the aqueous cleaners which increases the polarity of the surface, thereby increasing epoxy-to-metal bond strengths. This silicate layer probably also provides a measure of corrosion protection. The semi-aqueous cleaner Axarel 52, on the other hand, leaves behind a nonpolar carbonaceous layer which appears to reduce epoxy-to-metal bond strengths. The semi-aqueous cleaner Prima Clean was found to promote rusting of steel surfaces and was therefore dropped from consideration.

In cleaning efficiency studies, it appeared that Jettacin and Axarel 52 removed process soils somewhat more efficiently than Brulin 815 GD and Metalube 4U. (However, Axarel 52 leaves its own carbonaceous residue which more than compensates for its apparently good cleaning efficiency.) It cannot be said at this point, however, which cleaners clean "best" since only one set of process conditions per cleaner was studied, and the conditions were different for different cleaners. More definitive studies involving a wide range of process conditions are underway on two of the cleaners (Jettacin and Brulin 815 GD). These studies will provide a more sound basis for the final down-selection.

5.0 ACKNOWLEDGMENTS

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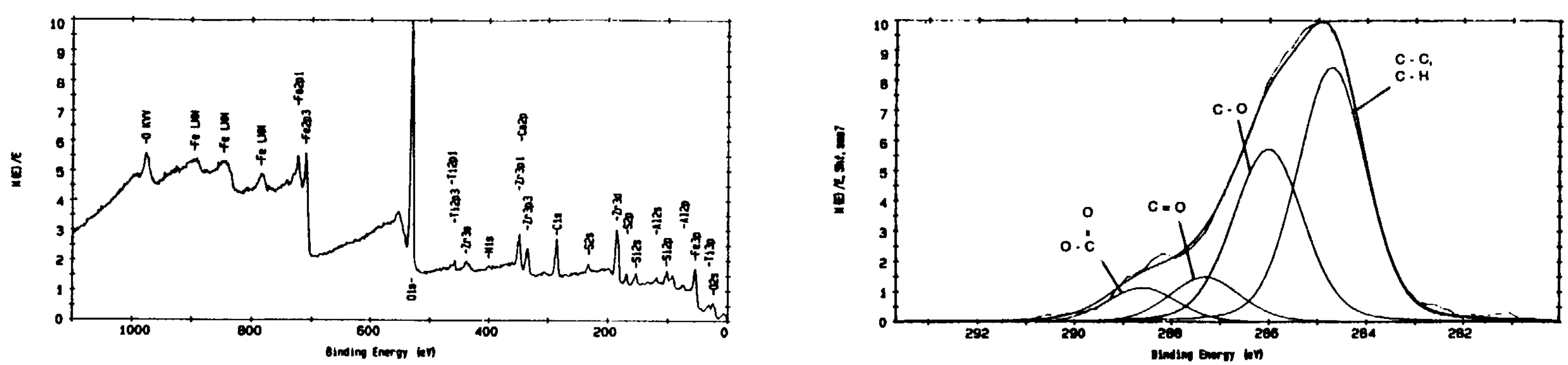

Figure 1. ESCA Spectra of Uncontaminated D6AC Steel. Left: Survey. Right: High Resolution Carbon (1s) Scan.

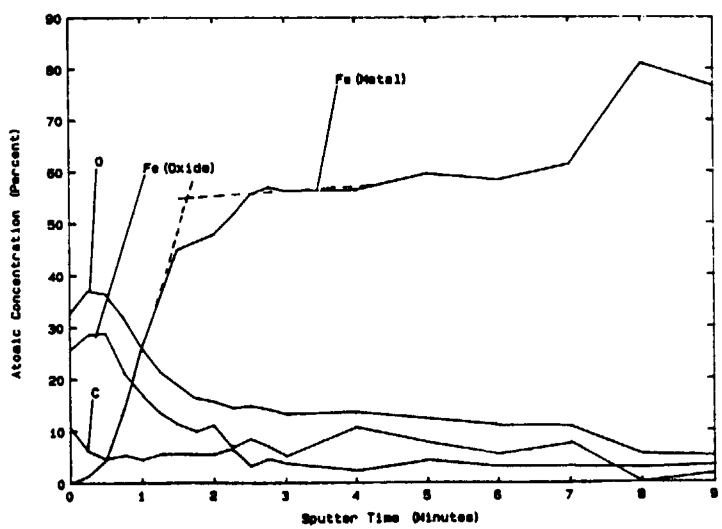

Figure 2. AES Depth Profile of Uncontaminated D6AC Steel

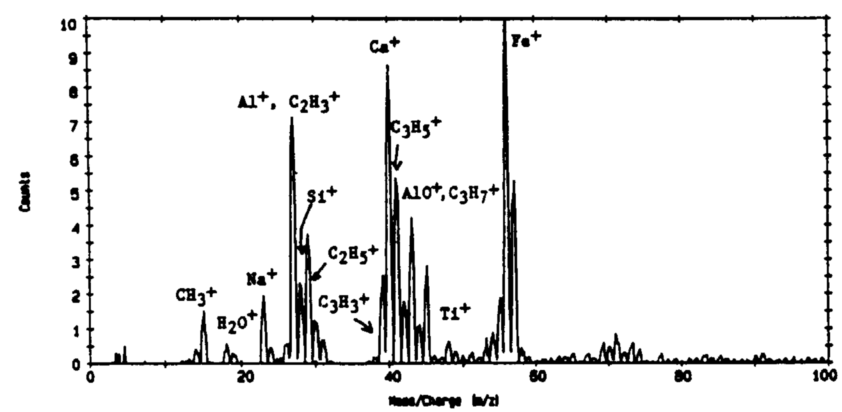

Figure 3. Static SIMS Spectrum (Positive Ions)
of Uncontaminated D6AC Steel

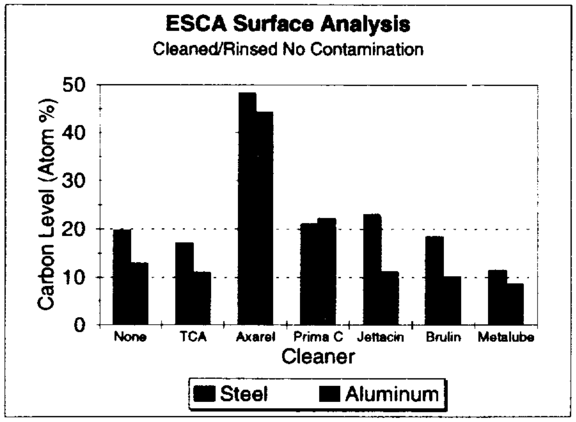

Figure 4. ESCA Carbon Levels on Cleaned/Rinsed Steel and Aluminum

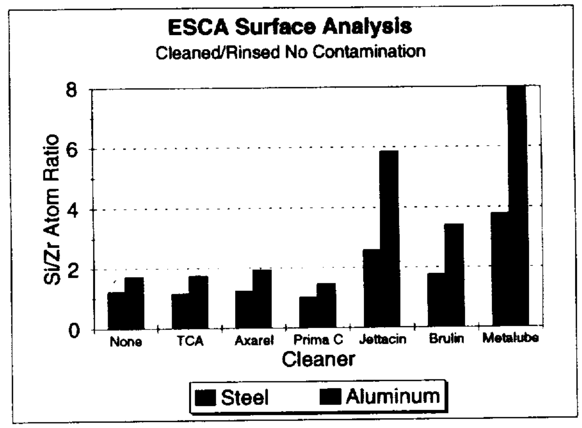

Figure 5. ESCA Silicon Levels on Cleaned/Rinsed Steel and Aluminum

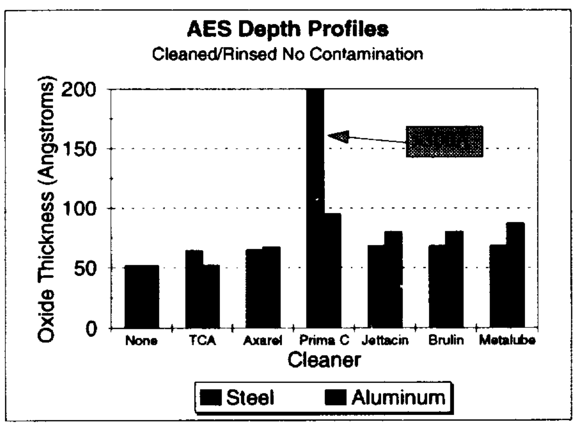

Figure 6. AES Oxide Thickness of Cleaned/Rinsed Steel and Aluminum

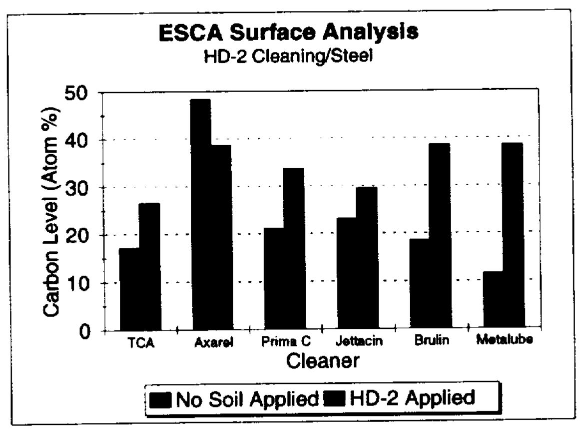

Figure 7. HD-2 Grease Cleaning Efficiency (Steel)

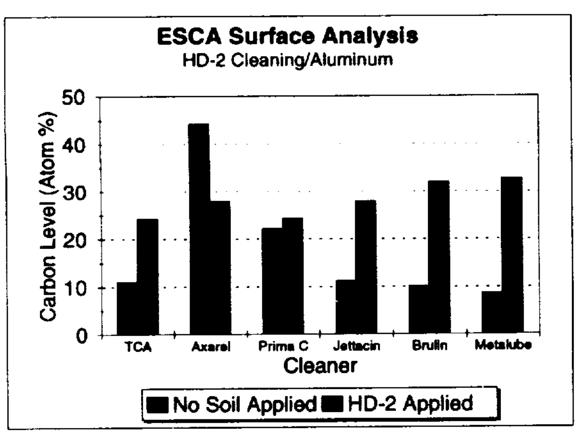

Figure 8. HD-2 Grease Cleaning Efficiency (Aluminum)

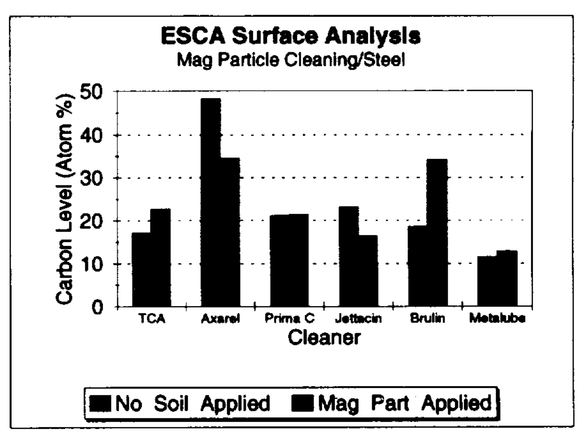

Figure 11. Magnetic Particle Cleaning Efficiency (Steel)

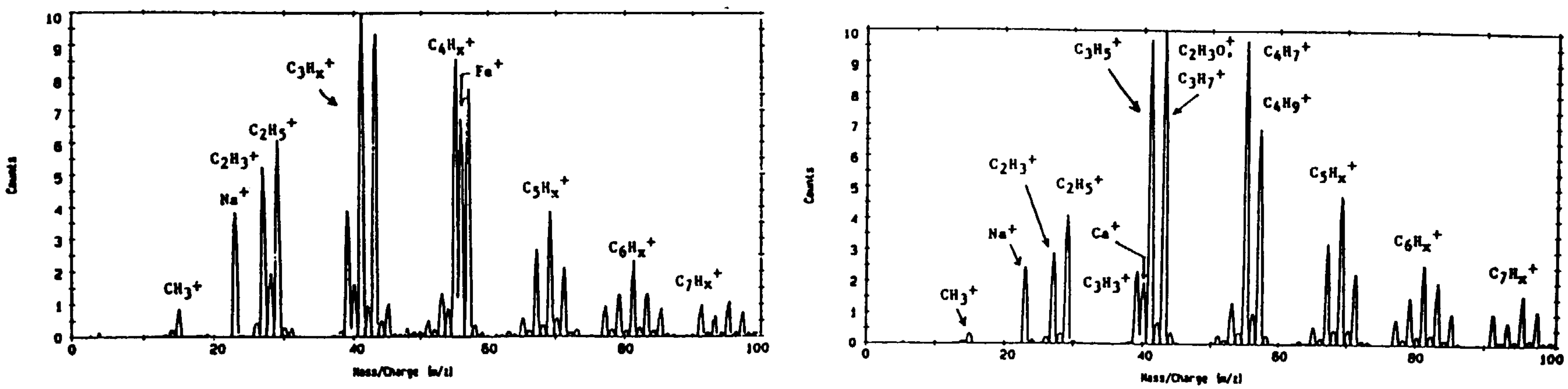

Figure 9. Static SIMS Spectra of (left) HD-2 Contaminated, Metalube 4U Cleaned Steel; (right) Pure HD-2 Grease Reference.

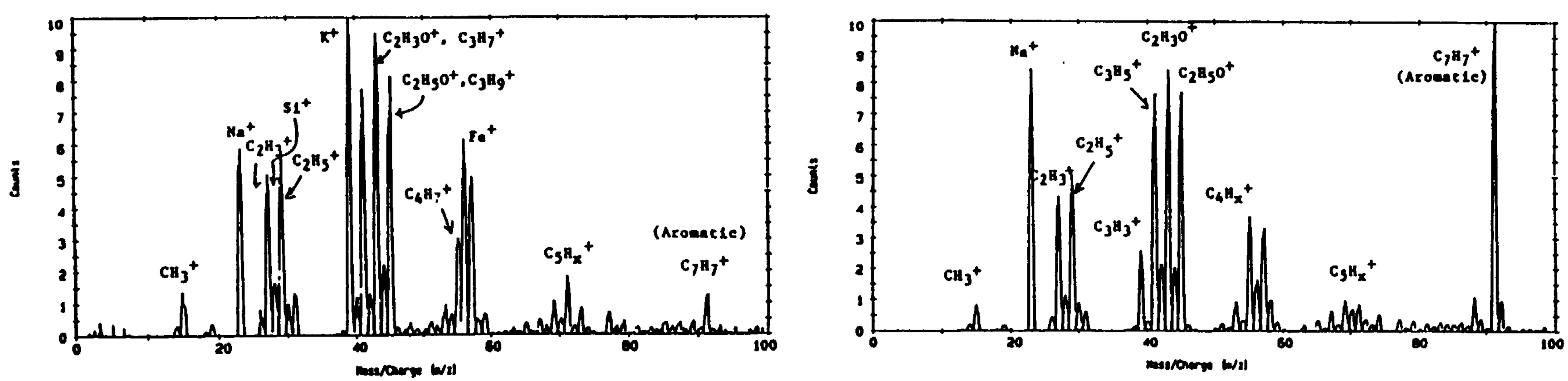

Figure 10. Static SIMS Spectra of (left) Mag Particle Contaminated, Brulin 815GD Cleaned Steel; (right) Pure Magnaglo WA-4 Reference.

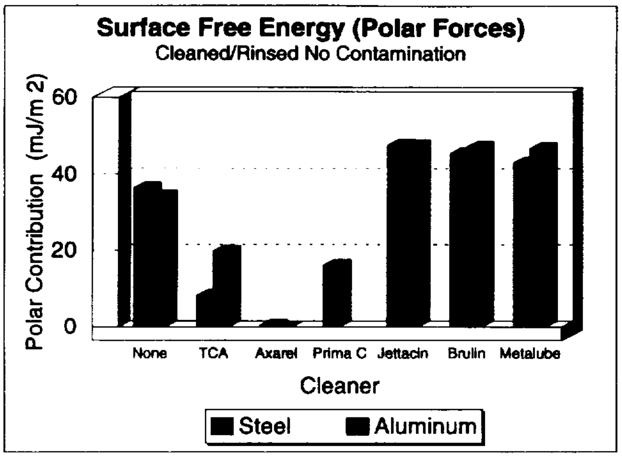

Figure 12. Surface Free Energy (Polar Contribution) of Cleaned/Rinsed Steel and Aluminum

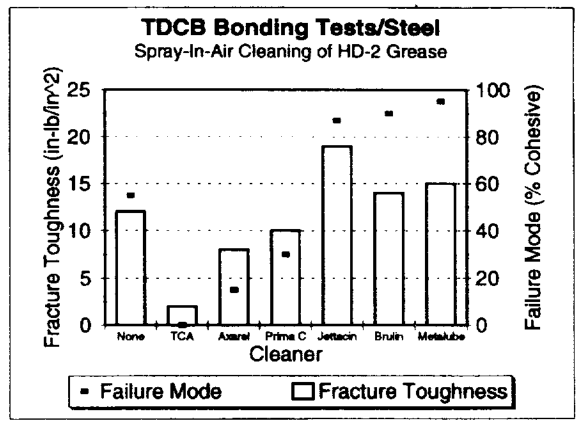

Figure 13. Fracture Toughness Results for HD-2 Contaminated, Cleaned Steel (EA-913NA Epoxy Adhesive)

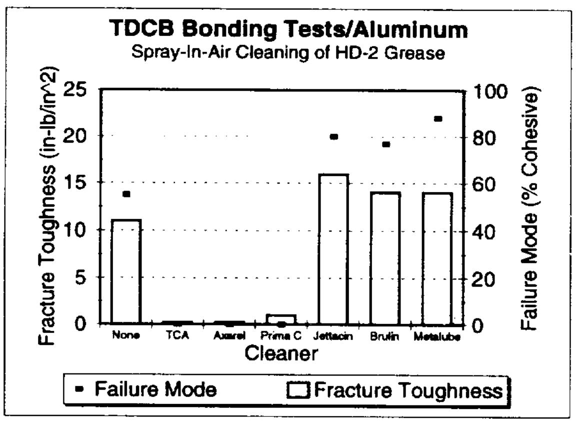

Figure 14. Fracture Toughness Results for HD-2 Contaminated, Cleaned Aluminum (EA-913NA Epoxy Adhesive)

Table I

ESCA Surface Analysis of D6AC Steel Coupons Cleaned But Not Rinsed

Surface Concentration (Atom %)														
Cleaner	Fe	O	Ti	N	Ca	Zr	C	S	Si	Al	Cl	K	P	Na
Steel Control	11.0	50.9	1.0	0.8	2.1	4.4	19.8	2.4	5.4	2.3	--	--	--	--
TCA Vapor	12.6	52.7	0.9	0.4	2.2	3.8	17.1	2.2	4.4	2.0	1.6	--	--	--
Axarel 52	3.8	32.2	0.2	--	0.1	1.9	56.6	0.1	1.8	0.6	0.0	--	2.6	--
Prima Clean	12.9	40.9	--	0.2	--	0.2	45.6	--	0.1	0.1	0.1	--	--	--
Jettacin	0.1	21.3	--	0.8	--	0.1	69.2	1.9	0.8	0.0	0.0	--	--	5.7
Brulin 815GD	0.9	26.7	0.2	2.5	0.1	1.0	60.4	0.2	3.3	0.4	--	1.5	2.6	0.2
Metalube 4U	--	27.5	--	1.9	--	0.1	59.7	3.6	1.2	--	--	0.2	--	5.9

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